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Emma Young
University of Wollongong, ely677@uow.edu.au

Clare Paton-Walsh
University of Wollongong, clarem@uow.edu.au

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Abstract

The 'Black Saturday' fires were a series of devastating bushfires that burned across Victoria, Australia, during February 2009. The smoke plume from Saturday the 7th February, the worst day of the fires, separated from subsequent emissions and persisted for several weeks, providing the opportunity to track the changing composition of the smoke plume as it aged. In this study we have used satellite data from the Ozone Monitoring Instrument (OMI) and the Atmospheric InfraRed Sounder (AIRS) to characterise the emissions of formaldehyde and nitrogen dioxide from the fires. Emission ratios with respect to carbon monoxide are determined for formaldehyde (0.017 ± 0.004 mol.mol-1) and nitrogen dioxide (0.004 ± 0.001 mol.mol-1). Additionally OMI UV Aerosol Index is used to track the smoke plume and infer how the concentration of these gases changes as the smoke ages. Our study suggests that formaldehyde concentrations within the smoke plume increase during the first day before declining to background levels within 2 days after emission. Nitrogen dioxide concentrations show a monotonic decrease reaching background levels about 1 day after emission.

Keywords

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Formaldehyde and nitrogen dioxide in smoke plumes from Australia's Black Saturday fires

E L Young and C Paton-Walsh

School of Chemistry, University of Wollongong, Wollongong, NSW, Australia

E-mail: ely677@uow.edu.au, clarem@uow.edu.au

Abstract. The 'Black Saturday' fires were a series of devastating bushfires that burned across Victoria, Australia, during February 2009. The smoke plume from Saturday the 7th February, the worst day of the fires, separated from subsequent emissions and persisted for several weeks, providing the opportunity to track the changing composition of the smoke plume as it aged. In this study we have used satellite data from the Ozone Monitoring Instrument (OMI) and the Atmospheric InfraRed Sounder (AIRS) to characterise the emissions of formaldehyde and nitrogen dioxide from the fires. Emission ratios with respect to carbon monoxide are determined for formaldehyde (0.017 ± 0.004 mol.mol^{-1}) and nitrogen dioxide (0.004 ± 0.001 mol.mol^{-1}). Additionally OMI UV Aerosol Index is used to track the smoke plume and infer how the concentration of these gases changes as the smoke ages. Our study suggests that formaldehyde concentrations within the smoke plume increase during the first day before declining to background levels within 2 days after emission. Nitrogen dioxide concentrations show a monotonic decrease reaching background levels about 1 day after emission.

1. Introduction

Biomass burning is a major contributor to the release of trace gases and aerosols into the atmosphere. Some of the trace gases emitted by biomass burning contribute directly to global warming as "greenhouse" gases [1], others indirectly by influencing the abundance of hydroxyl radicals [2] and thus the atmospheric lifetimes of other "greenhouse" gases that react with them [3]. Several of the trace gases emitted by biomass burning can influence the acidity of precipitation [4] and both trace gases and aerosols can degrade air quality and pose a threat to human health [5]. Aerosols can also influence radiative transfer processes in the atmosphere through direct absorption and scattering, or indirectly as cloud condensation nuclei [4, 5].

Models of atmospheric composition require some measurement or estimate of the emissions from biomass burning [6]. Total emissions of a particular gas from fires are normally calculated as the product of the area burned, the average fuel load, the efficiency of combustion and the emission factor for the gas of interest, where the emission factor is the mass of a compound released per unit of dry matter consumed [6]. To determine emission factors directly, detailed field studies that include determination of the carbon content of the fuel are required. Alternatively an emission factor may be determined by measuring the emission ratio of the gas to a reference gas such as carbon monoxide (CO) or carbon dioxide (CO_2) and then multiplying by a previously measured emission factor for the reference gas [6]. Emission ratios are obtained by dividing the enhanced concentration of a trace gas by the enhanced concentration of a reference gas. "Enhanced" concentrations are obtained by subtracting ambient concentrations of the gases from those concentrations measured in the smoke

plume. The emission ratio can also be considered as the slope of the concentration of the species plotted against the concentration of the reference species [6].

The 'Black Saturday' bushfires were a series of devastating fires burning across Victoria on Saturday the 7th February 2009. At least 400 individual fires were ignited on the day and these continued to burn throughout the state until mid-March, when favourable weather conditions helped to extinguish them. The fires claimed 173 lives [7], which is Australia's largest ever death toll from a bushfire. The smoke plumes from the Black Saturday bushfires eluded the ground-based remote sensing spectrometers at the University of Wollongong, but were observed by numerous satellite-based sensors. In this study satellite data was used to determine emission ratios for formaldehyde (H_2CO) and nitrogen dioxide (NO_2) with respect to CO from the Black Saturday fires and examine how the ratio of these gases changed as the smoke plume aged. Descriptions of the satellite platforms and sensors included in the survey are given below.

The Ozone Monitoring Instrument (OMI) is one of four instruments aboard the NASA satellite Aura and records daily global measurements of backscattered solar radiation in the visible and ultra-violet. OMI can distinguish between aerosol types such as smoke, dust and sulfates based upon differences in spectral absorbance and geographical location [8]. The UV Aerosol Index is derived from OMI measurements and is an indicator of near-UV absorbing aerosols such as smoke [9]. The index measures the deviation of an observed spectrum from the ideal molecular atmosphere as influenced by the presence of UV absorbing aerosols [10]. The mapped index over the period from the 7th February 2009 to the 3rd March 2009 shows the smoke plume from the original Victorian Black Saturday bushfires form and then separate from subsequent emissions. The plume then appears to be transported to the north of New Zealand where it lingered for over a week before it travelled west over northern Australia, and eventually dissipated completely over the Indian Ocean nearly a month later. The UV Aerosol Index can therefore be useful as a tracer of regional aerosol transport.

OMI also gathers spectral information that can be used to determine column amounts of trace gases such as H_2CO (measured at spectral resolution of ~0.45 nm in the UV-2: 310-365nm) [11, 12] and NO_2 (measured at spectral resolution of ~0.63 nm in the visible: 350-500nm) [11, 12] that are used in this study [13]. OMI differentiates trace gases by measuring backscattered solar radiation at known optimal wavelengths for individual gas species [11]. A combination of processing algorithms are used to extract OMI data products including TOMS Version 8, DOAS (Differential Optical Absorption Spectroscopy), Hyperspectral BUV retrievals and forward modelling [14].

The Atmospheric InfraRed Sounder (AIRS) is carried aboard NASA's Aqua satellite. AIRS measures the infrared energy from the Earth's surface, separating wavelengths which are each sensitive to variants such as temperature, water vapour and some trace gases [15, 16]. Of particular interest to this study, is the instrument's ability to measure the abundance of CO in the atmosphere.

2. Deriving Emission Ratios from OMI and AIRS data

Maps visualizing daily OMI UV Aerosol Index from 7th February 2009- 3rd March 2009 were obtained from the Giovanni online data system [17]. H_2CO and NO_2 total column amounts were obtained from the OMI sensor onboard the satellite Aura (Level 2 data products were used). For CO, the total column amounts from the AIRS instrument onboard the satellite Aqua were used (ascending swaths – Level 3 data products).

The daily mapped column amounts for the reference gas, CO, were used to define the region of the active fires by limiting analyses to areas where CO concentration was enhanced on each individual day. The column amount data for CO from the 7th February showed insufficient enhancements for an emission ratio to be determined. The lack of enhancement in CO concentration could be attributed to the possibility that the smoke plume had yet to develop strongly on the 7th February, as most of the major fires had only just begun on this day. Total column amount averages of H_2CO and NO_2 from the 8th, 9th and 10th of February 2009 for each grid space (1^o latitude by 1^o longitude) in the defined areas were plotted against the co-located total column amounts of CO. The gradient of the best straight line fit (using a linear regression) to these points gave the emission ratio of each gas relative to CO. The

standard deviation of the gradient was taken as an estimate of the uncertainty in the calculated emission ratio. It should be noted that the quoted uncertainties are from statistical analysis that assumes that the uncertainties in each point are uncorrelated. Since this is not the case the true uncertainty is likely to be larger. In addition, firestorms can cause cloud to develop and this smoke and cloud could degrade the instruments' abilities to measure below the height of the top of the plume adding to the uncertainty of the measurements.

There were significantly enhanced concentrations of CO, H_2CO and NO_2 over the active fire region on the 8th February 2009. Data from this day yielded emission ratios with respect to CO of 0.004 ± 0.001 mol.mol^{-1} for NO_2 with a correlation coefficient of 0.81; and 0.017 ± 0.004 mol.mol^{-1} for H_2CO with a correlation coefficient of 0.81 (see Figure 1 for the plots from which these emission ratios were derived). OMI H_2CO and NO_2 total column amounts were poorly correlated with AIRS CO total columns on the 9th and 10th February 2009. There appeared to be a significant fraction of OMI data missing over the relevant areas, especially on the 9th February, leading to increased uncertainties when averaging over the 1° latitude by 1° longitude grid spaces.

There are no previous measurements of emission ratios or emission factors for NO_2 from Australian temperate forest fires in the literature and results for different types of vegetation and in different climatic regions of the world vary by several orders of magnitude [6, 18].

The emission ratio for H_2CO with respect to CO from the 8th February 2009 is in broad agreement with emission ratios from *Paton-Walsh et al* (0.019 ± 0.008 mol.mol^{-1} [19] and 0.023 ± 0.007 mol.mol^{-1} [20]) and with *Andreae and Merlot's* emission factor (2.2 ± 0.5 g/kg) assuming their mean emission factor for CO for extratropical forests of 107 ± 37 g/kg [6].

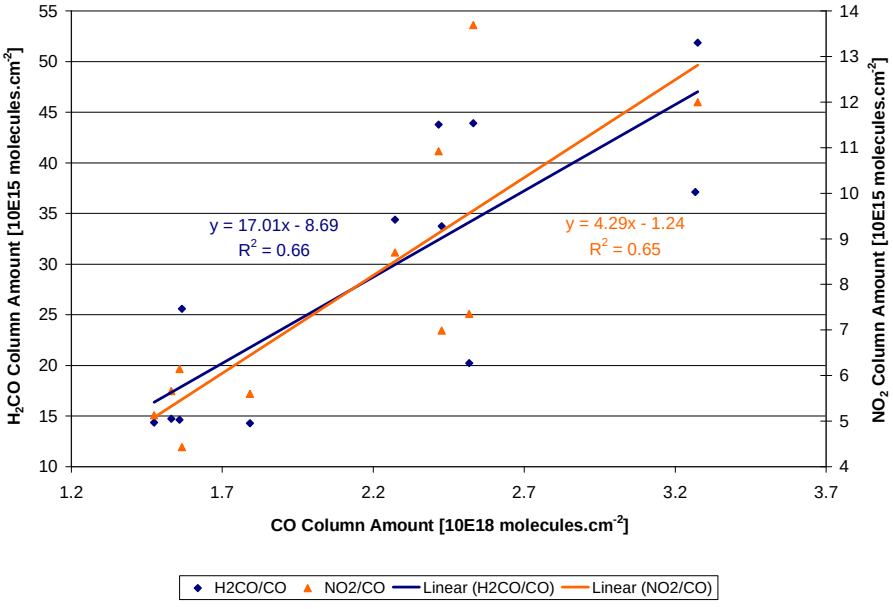

Figure 1: H_2CO and NO_2 column amounts plotted against CO column amounts to derive emission ratios for the active fires on the 8th February 2009.

3. Characterising the Aging of the Smoke Plume Using Changing Emission Ratio Values

OMI UV Aerosol Index was used to track the movement of the smoke plume that was emitted from the first fires and thereby to define the analysis regions for the evolution of the trace gases H_2CO, NO_2 and CO. Figure 2a shows enhanced OMI UV Aerosol Index revealing the location of the smoke plume on the 8th February 2009. Gaps in the data to the edge of each satellite swath artificially break up the plume into three areas, one that is close to and incorporates the active fire region, the main section that extends across the south island of New Zealand and a small region to the east of New Zealand. On the 9th and 10th of February 2009 the smoke plume is located to the northeast of New Zealand's north island. Emission ratios were calculated using OMI H_2CO and NO_2 and AIRS CO total column data

over the region of the travelling plume on the 9th and 10th February 2009 and separately for the two largest of the three separate regions identified on the 8th February 2009, the "active fire" grid and the main section or "Area 2".

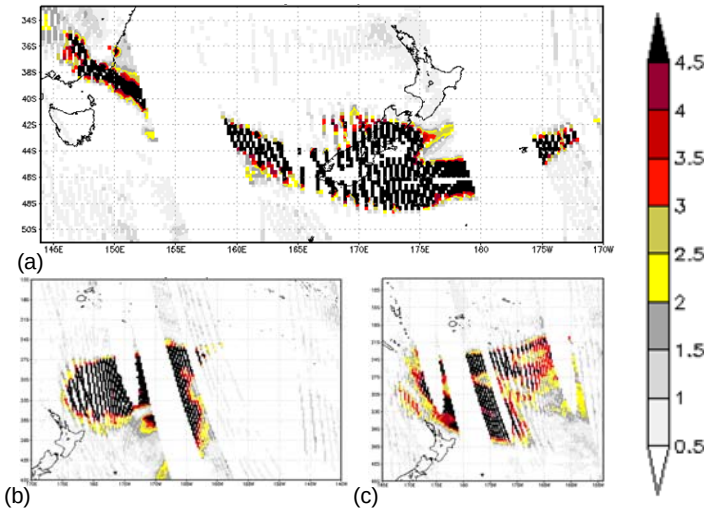

Figure 2: The mapped product of the UV Aerosol Index data on (a) the 8th February 2009 (144E-170W, 33S-51S), (b) the 9th February 2009 (170E-140W, 15S-45S) and (c) the 10th February 2009 (165E-154W, 10S-45S) for the travelling plume. The coloured area of enhanced aerosol in each map represents the area within which data analysis for the trace gases was concentrated on each day.

The total column amounts of H_2CO and NO_2 derived from OMI spectra over the region of the smoke plume showed no significant enhancements after the 10th February 2009. This is because H_2CO and NO_2 are highly reactive with atmospheric lifetimes of the order of hours [21]. In comparison CO has a lifetime in the order of 2 months [22] and so changes in the emission ratio of H_2CO and NO_2 with respect to CO as the smoke ages will be dominated by the rapid changes in the reactive gases. Figure 3 shows the changing emission ratios of H_2CO and NO_2 as the smoke aged from the youngest smoke measured over the active fire area on the 8th February 2009 to the oldest smoke measured to the north of New Zealand on the 10th February 2009. The emission ratios of each gas go to zero at background levels since an emission ratio is the *enhanced* concentration of the trace gas divided by the *enhanced* concentration of a reference gas.

The pseudo time-series of NO_2 emission ratios shown in Figure 3b reveals a rapid decline with age in the Black Saturday smoke plume. NO_2 declines with respect to CO from 0.004 ± 0.001 mol.mol^{-1} on the 8th February over the active fire, to near background levels over Area 2 on the 8th February and over the areas of the 9th and 10th February when considering the levels of uncertainty. This decline is likely to be a symptom of the numerous destructive reactions that NO_2 undergoes in the atmosphere. For example, NO_2 oxidises to nitrates, is photolysed during the day to NO and reacts with a number of compounds including $OH^{\cdot}$, HO_2, ClO and BrO [22].

H_2CO is released as a direct product of biomass burning but it has a lifetime of approximately three hours in daylight [21]. This is largely due to destruction by photolysis or reaction with the hydroxyl radical. To a lesser extent, H_2CO reacts with NO_3 resulting in abstraction of a hydrogen atom, aqueous conversion of H_2CO results in formic acid and the addition of HO_2 destroys H_2CO and forms the hydroxyl methyl peroxy radical [22].

Based on its short lifetime as a consequence of destructive reactions, it could be expected that the concentration of H_2CO would appear highest on the 8th February, particularly over the area of the active fires where the emissions were the freshest. Whilst the emission ratio of H_2CO to CO was high over this area (0.017 ± 0.004 mol.mol^{-1}), further emission ratios revealed that the concentration of H_2CO was highest on the 8th February over Area 2 (the emission ratio was 0.024 ± 0.003 mol.mol^{-1}), where the smoke was slightly older, having travelled further from the site of the fires. The high uncertainties in the derivation of emission ratios mean that the increase may not be statistically significant; however, such an increase could result from reactive sources of H_2CO from within the plume itself. H_2CO is a known product of the oxidation of many hydrocarbons that would be

prominent in a smoke plume [21, 22]. In particular, model studies have indicated that non methane volatile organic compounds (NMVOCs) such as acetic acid, methanol and ethene can be a significant secondary source of H_2CO in smoke; these compounds are estimated to account for 43 percent of final H_2CO production [23]. It is also possible that the larger H_2CO to CO ratio calculated for the older part of the smoke plume on the 8th February (Area 2) resulted from a greater original emission ratio from the earlier stages of the active fires. This is plausible because the earliest fires would be expected to be dominated by flaming combustion, and CO is associated more with smouldering phase whilst H_2CO can be associated with both flaming and smouldering combustion [24].

The emission ratios on the 9th and 10th February reveal a subsequent decrease in the amount of H_2CO within the plume as it ages. By these days the composition of H_2CO had decreased to background levels within the respective uncertainties of the estimates, indicating that the excess H_2CO from the fires and possible resultant reactions within the plume had disappeared.

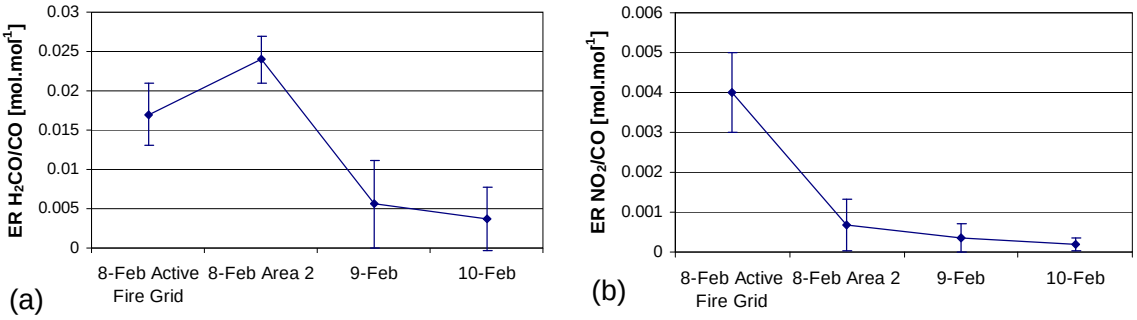

Figure 3: Emission ratios with respect to CO for (a) H_2CO and (b) NO_2, plotted as a "pseudo time-series" as the smoke ages from the youngest smoke measured over the active fire area on the 8th February 2009 to the oldest smoke measured to the north of New Zealand on the 10th February 2009.

4. Conclusions

OMI UV Aerosol Index has been used to track the smoke plume emitted from the Black Saturday bushfires. Comparison of the changing column amounts of H_2CO and NO_2 from OMI with CO columns from AIRS reveals information about the changing composition of the smoke plume as it ages. Large enhancements in all three of these trace gases were observed in the plume. NO_2 column amounts exhibited a rapid decline with time, whilst H_2CO column amounts peaked once the plume had begun to age, then declined and eventually dissipated after the third day. The increase after aging may be attributed to reactive sources of the trace gas from within the plume itself.

Emission ratios with respect to CO from the fires of 0.017 ± 0.004 mol.mol^{-1} for H_2CO and 0.004 ± 0.001 mol.mol^{-1} for NO_2 were determined. This emission ratio for H_2CO is in broad agreement with previous values in the literature. The result for NO_2 is especially significant because it is the first measurement of an emission ratio for this important gas from Australian forest fires.

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